

UV STABILIZING ADDITIVE COMPOSITIONFIELD OF THE INVENTION

5 This invention relates to an improved UV stabilizing additive composition. More specifically, this invention relates to an UV stabilizing additive composition comprising an ortho-hydroxy triazine compound, a hindered amine compound and hydroxybenzophenone compound.

10 BACKGROUND OF THE INVENTION

Exposure to sunlight and other sources of ultraviolet (UV) radiation is known to cause degradation of a wide variety of materials, especially polymeric materials. For example, polymeric materials such as plastics often discolor, lose gloss and/or become brittle as a result of prolonged exposure to UV light due primarily to a reduction in the molecular weight of 15 the polymer. Accordingly, a large body of art has been developed directed towards materials such as UV light absorbers and stabilizers, which are capable of inhibiting such degradation in polymeric articles.

20 The present inventors have found that a combination of ortho-hydroxy triazine compound, a hindered amine compound and hydroxybenzophenone compound provides synergistic protection of materials against UV light. This combination either provides better protection at typical UV stabilizer loading levels, or typical protection at much lower loading levels resulting in significant cost savings over prior art UV stabilizing additive compositions.

SUMMARY OF THE INVENTION

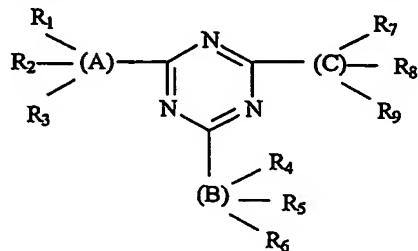
25 This invention relates to an UV stabilizing additive composition comprising an ortho-hydroxy triazine compound, a hindered amine compound and a hydroxybenzophenone compound. This additive composition may be used to stabilize materials from UV radiation. This invention also contemplates a method of stabilizing a material by contacting the 30 material with the UV stabilizing additive composition.

DETAILED DESCRIPTION OF THE INVENTION

This invention relates to an UV stabilizing additive composition comprising an ortho-hydroxy triazine compound, a hindered amine light stabilizing (HALS) compound and a 35 hydroxybenzophenone compound.

Preferably, the ortho-hydroxy tris-aryl-s-triazine compound has the following formula I:

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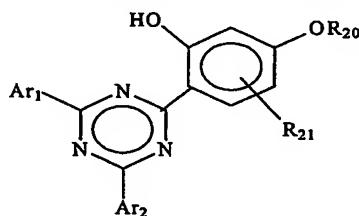


where A, B and C are each aromatic, at least one of A, B and C is substituted by a hydroxy group ortho to the point of attachment to the triazine ring, and each of R₁ through R₉ is selected from the group consisting of hydrogen, hydroxy, alkyl, alkoxy, sulfonic, carboxy, halo, haloalkyl and acylamino having from about 1 to about 24 carbon atoms.

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One embodiment of the tris-aryl-s-triazine is a compound having the formula II:

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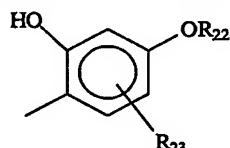


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where Ar₁ and Ar₂ are the same or different and are substituted or unsubstituted aryl groups; and where R₂₀ and R₂₁ are each independently a hydrogen, C₁-C₂₄ alkyl, C₁-C₂₄ haloalkyl, C₆-C₂₄ aryl, C₂-C₂₄ alkenyl, C₁-C₂₄ acyl, C₁-C₂₄ cycloalkyl, C₅-C₂₄ cycloacyl, C₇-C₂₄ aralkyl, or C₆-C₂₄ aracyl, substituted or unsubstituted biphenylene, substituted or unsubstituted napthalene, OR, NRR', CONRR', OCOR, CN, SR, SO₂R, and where R and R' are each independently a hydrogen, C₁-C₂₄ alkyl, C₁-C₂₄ haloalkyl, C₆-C₂₄ aryl, C₂-C₂₄ alkenyl, C₁-C₂₄ acyl, C₁-C₂₄ cycloalkyl, C₅-C₂₄ cycloacyl, C₇-C₂₄ aralkyl, or C₆-C₂₄ aracyl, substituted or unsubstituted biphenylene, or substituted or unsubstituted napthalene.

Preferably, in the above formula II, Ar₁ has the formula IIa:

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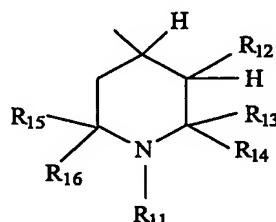
where R₂₂ and R₂₃ are each independently a hydrogen, C₁-C₂₄ alkyl, C₁-C₂₄ haloalkyl, C₆-C₂₄ aryl, C₂-C₂₄ alkenyl, C₁-C₂₄ acyl, C₁-C₂₄ cycloalkyl, C₅-C₂₄ cycloacyl, C₇-C₂₄ aralkyl, or C₆-C₂₄ aracyl, substituted or unsubstituted biphenylene, substituted or unsubstituted napthalene, OR, NRR', CONRR', OCOR, CN, SR, and SO₂R, and where R and R' are as defined above.

Also preferred in the above formula II is when R₂₀ is hydrogen or a C₁-C₈ alkyl, R₂₁ is hydrogen and Ar₁ and Ar₂ may be the same or different and are benzyl, methylbenzyl, or dimethylbenzyl.

Examples of suitable tris-aryl-s-triazines that may be used are 2,4,6-tris(2-hydroxy-4-octyloxyphenyl)-1,3,5-triazine; 2-(2-hydroxy-4-n-octyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine; 2-(2-hydroxy-4-(mixed iso-octyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine; 2-(2,4-dihydroxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine; 2,4-bis(2-hydroxy-4-propyloxyphenyl)-6-(2,4-dimethylphenyl)-1,3,5-triazine; 2-(2-hydroxy-4-octyloxyphenyl)-4,6-bis(4-methylphenyl)-1,3,5-triazine; 2-(2-hydroxy-4-dodecyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine; 2-(2-hydroxy-4-tridecyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine; 2-[2-hydroxy-4-(2-hydroxy-3-butyloxypropoxy)phenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine; 2-[2-hydroxy-4-(2-hydroxy-3-octyloxypropoxy)-phenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine; 2-[4-dodecyloxy/tridecyloxy-2-hydroxypropoxy)-2-hydroxyphenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine; 2-[2-hydroxy-4-(2-hydroxy-3-dodecyloxypropoxy)phenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine; 2-(2-hydroxy-4-hexyloxy)phenyl-4,6-diphenyl-1,3,5-triazine; 2-(2-hydroxy-4-methoxyphenyl)-4,6-diphenyl-1,3,5-triazine; 2,4,6-tris[2-hydroxy-4-(3-butoxy-2-hydroxypropoxy)phenyl]-1,3,5-triazine and 2-(2-hydroxyphenyl)-4-(4-methoxyphenyl)-6-phenyl-1,3,5-triazine.

The hindered amine compound may be any suitable hindered amine compound such as those containing a 2,2,6,6-tetraalkylpiperidine or 2,2,6,6-tetraalkylpiperazinone radical. One embodiment of a hindered amine compound is one that contains at least one group having the following formula III:

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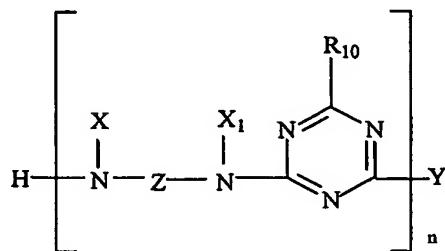


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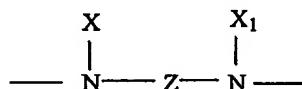
where R₁₁ is hydrogen, O, OH, C₁-C₁₈ alkyl, -CH₂CN, C₁-C₁₈ alkoxy, C₁-C₁₈ hydroxyalkoxy, C₅-C₁₂ cycloalkoxy, C₅-C₁₂ hydrocycloalkoxy, C₃-C₆ alkenyl, C₁-C₁₈ alkynyl, C₇-C₉ phenylalkyl, unsubstituted or substituted on the phenyl with 1, 2 or 3 C₁-C₄ alkyls, or an aliphatic C₁-C₈ acyl; R₁₂ is hydrogen, C₁-C₈ alkyl, or benzyl; R₁₃, R₁₄, R₁₅, and R₁₆ are each independently a C₁-C₁₈ alkyl, benzyl or phenethyl, or optionally R₁₃ and R₁₄, and/or R₁₅ and R₁₆, taken together with the carbon which they are attached, form a C₅-C₁₀ cycloalkyl.

Another embodiment of a hindered amine compound is a compound that has formula IV below:

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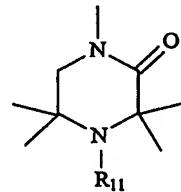
10 where R_{10} is a morpholino, $C_1 - C_8$ alkylamine, di($C_1 - C_8$) alkylamine, pyrrolidyl, cyclohexylamine or combinations thereof,
 X and X_1 , which may be the same or different, and are hydrogen, $C_1 - C_{20}$ alkyl, or a radical of formula III defined above,
 R_{11} to R_{16} are as defined above,
15 Z is a straight chained or branched $C_1 - C_{20}$ alkylene or a straight chained or branched $C_1 - C_{20}$ alkylene chain interrupted by at least oxy, thio, or $-N(R_{17})-$, where R_{17} is hydrogen, $C_1 - C_{20}$ alkyl, $C_5 - C_{10}$ cycloalkylene $C_6 - C_{12}$ arylene, $C_8 - C_{14}$ aralkylene or the radical of formula III;
 n is an integer greater than 1;
20 and Y is a halogen atom, $C_1 - C_8$ alkylamine, di($C_1 - C_8$) alkylamine, pyrrolidyl, morpholino, cyclohexylamine, or



25 where X , X_1 , and Z are as previously defined.

Preferably in the above formula IV, Z is a C_2 to C_8 alkylene, R_{10} is a morpholino or cyclohexylamine, X and X_1 is the radical of formula III, R_{11} is hydrogen or methyl, R_{12} is hydrogen, and R_{13} , R_{14} , R_{15} and R_{16} are methyl.

30 Another embodiment of a hindered amine is a 2,2,6,6-tetraalkylpiperazinone. One embodiment of a 2,2,6,6-tetraalkylpiperazinone compound is one that contains at least one group of formula IVa:



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where R_{11} is as defined above.

Examples of suitable hindered amine compounds include, but are not limited to:

1H-Pyrrole-2,5-dione, 1-octadecyl-, polymer with (1-methylethenyl)benzene and 1-(2,2,6,6-tetramethyl-4-piperidinyl)-1H-pyrrole-2,5-dione; piperazinone, 1,1',1"-[(1,3,5-triazine-2,4,6-triyltris[(cyclohexylimino)-2,1-ethanediyl]])tris[3,3,5,5-tetramethyl-]]; piperazinone, 1,1',1"-[(1,3,5-triazine-2,4,6-triyltris[(cyclohexylimino)-2,1-ethanediyl]])tris[3,3,4,5,5-pentamethyl-]];
5 the reaction product of 7,7,9,9-tetramethyl-2-cycloundecyl-1-oxa-3,8-diaza-4-oxospiro[4.5]decane and epichlorohydrin; the condensate of N,N'-bis(2,2,6,6-tetramethylpiperidin-4-yl)hexamethylenediamine and 4-cyclohexylamino-2,6-dichloro-1,3,5-triazine; the condensate of 1,2-bis(3-aminopropylamino)ethane; 2,4,6-trichloro-1,3,5-triazine
10 and 4-butylamino-2,2,6,6-tetramethylpiperidine; the condensate of N,N'-bis(2,2,6,6-tetramethylpiperidin-4-yl)hexamethylenediamine and 4-morpholino-2,6-dichloro-1,3,5-triazine; the condensate of 2-chloro-4,6-bis(4-n-butylamino-2,2,6,6-tetramethylpiperidyl)-1,3,5-triazine and 1,2-bis(3-aminopropylamino)ethane; the condensate of 2-chloro-4,6-bis(4-n-butylamino-1,2,2,6,6-pentamethylpiperidyl)-1,3,5-triazine and 1,2-bis-(3-aminopropylamino)ethane; 2-[(2-hydroxyethyl)amino]-4,6-bis[N-(1-cyclohexyloxy-2,2,6,6-tetramethylpiperidin-4-yl)butylamino-1,3,5-triazine; propanedioic acid, [(4-methoxyphenyl)methylene]-bis-(1,2,2,6,6-pentamethyl-4-piperidinyl) ester; tetrakis(2,2,6,6-tetramethylpiperidin-4-yl)-1,2,3,4-butanetetracarboxylate; benzenepropanoic acid, 3,5-bis(1,1-dimethylethyl)-4-hydroxy-, 1-[2-[3-[3,5-bis(1,1-dimethylethyl)-4-hydroxyphenyl]-1-oxopropoxy]ethyl]-2,2,6,6-tetramethyl-4-piperidinyl ester; N-(1-octyloxy-2,2,6,6-tetramethylpiperidin-4-yl)-N'-dodecyloxalamide; tris(2,2,6,6-tetramethylpiperidin-4-yl)nitrioltriacetate; 1,5-dioxaspiro{5,5}undecane-3,3-dicarboxylic acid, bis(1,2,2,6,6-pentamethyl-4-piperidinyl); 1,5-dioxaspiro{5,5}undecane-3,3-dicarboxylic acid, bis(2,2,6,6-tetramethyl-4-piperidinyl); the condensate of 1-(2-hydroxyethyl)-2,2,6,6-tetramethyl-4-hydroxypiperidine and succinic acid; the condensate of N,N'-bis(2,2,6,6-tetramethylpiperidin-4-yl)hexamethylenediamine and 4-tert-octylamino-2,6-dichloro-1,3,5-triazine; 1,2,3,4-butanetetracarboxylic acid, 1,2,2,6,6-pentamethyl-4-piperidinyl tridecyl ester; tetrakis(2,2,6,6-tetramethylpiperidin-4-yl)-1,2,3,4-butanetetracarboxylate; 1,2,3,4-butanetetracarboxylic acid, 2,2,6,6-tetramethyl-4-piperidinyl tridecyl ester; tetrakis(1,2,2,6,6-pentamethylpiperidin-4-yl)-1,2,3,4-butanetetracarboxylate; mixture of 2,2,4,4-tetramethyl-21-oxo-7-oxa-3.20-diazaspiro(5.1.11.2)-heneicosane-20-propanoic acid-dodecylester; 2,2,4,4-tetramethyl-21-oxo-7-oxa-3.20-diazaspiro(5.1.11.2)-heneicosane-20-propanoic acid-tetradecylester; 1H,4H,5H,8H-2,3a,4a,6,7a,8a-hexaaazacyclopenta[def]fluorene-4,8-dione, hexahydro-2,6-bis(2,2,6,6-tetramethyl-4-piperidinyl); polymethyl[propyl-3-oxy(2',2',6',6'-tetramethyl-4,4'-piperidinyl)]siloxane; polymethyl[propyl-3-oxy(1',2',2',6',6'-pentamethyl-4,4'-piperidinyl)]siloxane; copolymer of methylmethacrylate with ethyl acrylate and 2,2,6,6-

tetramethylpiperidin-4-yl acrylate; copolymer of mixed C₂₀ to C₂₄ alpha-olefins and (2,2,6,6-tetramethylpiperidin-4-yl)succinimide; 1,2,3,4-butanetetracarboxylic acid, polymer with $\beta,\beta,\beta',\beta'$ -tetramethyl-2,4,8,10-tetraoxaspiro[5.5]undecane-3,9-diethanol, 1,2,2,6,6-pentamethyl-4-piperidinyl ester; 1,2,3,4-butanetetracarboxylic acid, polymer with $\beta,\beta,\beta',\beta'$ -

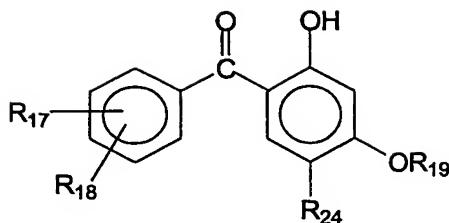
5 tetramethyl-2,4,8,10-tetraoxaspiro[5.5]undecane-3,9-diethanol, 2,2,6,6-tetramethyl-4-piperidinyl ester copolymer; 1,3-benzeneddicarboxamide, N,N'-bis(2,2,6,6-tetramethyl-4-piperidinyl; 1,1'-(1,10-dioxo-1,10-decanediyl)-bis(hexahydro-2,2,4,4,6-pentamethylpyrimidine; ethane diamide, N-(1-acetyl-2,2,6,6-tetramethylpiperidinyl)-N'-dodecyl; formamide, N,N'-1,6-hexanediylibis[N-(2,2,6,6-tetramethyl-4-piperidinyl); D-glucitol,

10 1,3:2,4-bis-O-(2,2,6,6-tetramethyl-4-piperidinylidene)-; 2,2,4,4-tetramethyl-7-oxa-3,20-diaza-21-oxo-dispiro[5.1.11.2]heneicosane; propanamide, 2-methyl-N-(2,2,6,6-tetramethyl-4-piperidinyl)-2-[(2,2,6,6-tetramethyl-4-piperidinyl)amino]-; 7-oxa-3,20-diazadispiro[5.1.11.2]heneicosane-20-propanoic acid, 2,2,4,4-tetramethyl-21-oxo-, dodecyl ester; N-(2,2,6,6-tetramethylpiperidin-4-yl)- β -aminopropionic acid dodecyl ester; N-(2,2,6,6-tetramethylpiperidin-4-yl)-N'-aminoxalamide; propanamide, N-(2,2,6,6-tetramethyl-4-piperidinyl)-3-[(2,2,6,6-tetramethyl-4-piperidinyl)amino]-; mixture of 4-hexadecyloxy- and 4-stearylxy-2,2,6,6-tetramethylpiperidine; 3-dodecyl-1-(1,2,2,6,6-pentamethylpiperidin-4-yl)pyrrolidine-2,5-dione; 3-dodecyl-1-(1-ethanoyl-2,2,6,6-pentamethylpiperidin-4-yl)pyrrolidine-2,5-dione; bis(2,2,6,6-tetramethylpiperidin-4-yl)succinate; bis(1,2,2,6,6-pentamethylpiperidin-4-yl) n-butyl 3,5-di-tert-butyl-4-hydroxybenzylmalonate; tris(2,2,6,6-tetramethylpiperidin-4-yl) nitrilotriacetate; 1,1'-(1,2-ethanediyl)bis(3,3,5,5-tetramethylpiperazinone); 4-benzoyl-2,2,6,6-tetramethylpiperidine; 4-stearylxy-2,2,6,6-tetramethylpiperidine; bis(1,2,2,6,6-pentamethylpiperidyl)-2-n-butyl-2-(2-hydroxy-3,5-di-tert-butylbenzyl)malonate; 3-n-octyl-7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]decan-2,4-dione;

15 bis(1-octyloxy-2,2,6,6-tetramethylpiperidyl)sebacate; bis(1-octyloxy-2,2,6,6-tetramethylpiperidyl)succinate; 8-acetyl-3-dodecyl-7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]decane-2,4-dione; 3-dodecyl-1-(2,2,6,6-tetramethylpiperidin-4-yl)pyrrolidin-2,5-dione; 3-dodecyl-1-(1-ethanoyl-2,2,6,6-tetramethylpiperidin-4-yl)pyrrolidine-2,5-dione; a mixture of 4-

20 hexadecyloxy- and 4-stearylxy-2,2,6,6-tetramethylpiperidine; 2-undecyl-7,7,9,9-tetramethyl-1-oxa-3,8-diaza-4-oxospiro[4.5]decane; 1,5-dioxaspiro{5,5}undecane-3,3-dicarboxylic acid, bis(2,2,6,6-tetramethyl-4-piperidinyl) and 1,5-dioxaspiro{5,5}undecane-3,3-dicarboxylic acid, bis(1,2,2,6,6-pentamethyl-4-piperidinyl).

25 The hydroxybenzophenone compound of the present invention may be any suitable hindered hydroxybenzoate compound such as those having the formula V:



where R₁₇, R₁₈ and R₂₄ are each independently hydrogen alkyl, aryl, aralkyl, alkaryl, alkoxy,

5 aryloxy having from 1 to 18 carbon atoms and R₁₉ is hydrogen, a C₁-C₂₄ alkyl, or substituted or unsubstituted C₆-C₂₄ aryl. Preferably, R₁₇, R₁₈ and R₂₄ are each hydrogen and R₁₉ is a C₁-C₈ alkyl.

Examples of suitable hindered hydroxybenzophenone compounds include:

2,4-dihydroxybenzophenone; 2-hydroxy-4-methoxybenzophenone; 2-hydroxy-4-
10 octyloxybenzophenone; 2-hydroxy-4-decyloxybenzophenone; 2-hydroxy-4-
dodecyloxybenzophenone; 2-hydroxy-4-benzyloxybenzophenone; 2,2'-dihydroxy-4,4'-
dimethoxybenzophenone; 2,2',4,4'-tetrahydroxybenzophenone; 2,4-dihydroxy-4'-tert-butyl-
benzophenone; 1,6-bis-(3-hydroxy-4-benzoylphenoxy)hexane; methylenebis-(2-benzoyl-5-
methoxyphenol).

15 In one embodiment of the present invention, the UV stabilizing additive composition of the present invention may be employed to stabilize materials which are subject to degradation by ultraviolet radiation by contacting the UV stabilizing additive composition with a composition comprising polymeric or other materials, either chemically or physically. Non-limiting examples of materials that may be so stabilized
20 are polyolefins, polyesters, polyethers, polyketones, polyamides, natural and synthetic rubbers, polyurethanes, polystyrenes, high-impact polystyrenes, polyacrylates, polymethacrylates, polyacetals, polyacrylonitriles, polybutadienes, polystyrenes, acrylonitrile-butadiene-styrene, styrene acrylonitrile, acrylate styrene acrylonitrile, cellulosic acetate butyrate, cellulosic polymers, polyimides, polyamideimides,
25 polyetherimides, polyphenylsulfides, polyphenyloxide, polysulfones, polyethersulfones, polyvinylchlorides, polycarbonates, polyketones, aliphatic polyketones, thermoplastic olefins, amino resin cross-linked polyacrylates and polyesters, polyisocyanate cross-linked polyesters and polyacrylates, phenol/formaldehyde, urea/formaldehyde and melamine/formaldehyde resins, drying and non-drying alkyd resins, alkyd resins,
30 polyester resins, acrylate resins cross-linked with melamine resins, urea resins, isocyanates, isocyanurates, carbamates, and epoxy resins, cross-linked epoxy resins

derived from aliphatic, cycloaliphatic, heterocyclic and aromatic glycidyl compounds, which are cross-linked with anhydrides or amines, polysiloxanes, Michael addition polymers, amines, blocked amines with activated unsaturated and methylene compounds, ketimines with activated unsaturated and methylene compounds, 5 polyketimines in combination with unsaturated acrylic polyacetooacetate resins, polyketimines in combination with unsaturated acrylic resins, radiation curable compositions, epoxymelamine resins, organic dyes, cosmetic products, cellulose-based paper formulations, photographic film paper, fibers, waxes, inks, and blends thereof.

Preferably, the materials to be stabilized are thermoplastic olefins, acrylonitrile-10 butadiene-styrene, polyesters, polyvinylchloride, polyamides, polyurethanes, or homo- and copolymers of propylene, isobutylene, butene, methylpentene, hexene, heptene, octene, isoprene, butadiene, hexadiene, dicyclopentadiene, ethylidene cyclopentene and norbornene. More preferably, the materials are polypropylene and thermoplastic olefins.

The amount of the triazine compound used in the material to be stabilized using the 15 combination of additives of the present invention is typically lower than normal usage. The lower limit of the amount of triazine may be as low as about 10 ppm, or about 20 ppm, or about 50 ppm or about 75 ppm or about 100 ppm or about 200 ppm, based on the amount of material to be stabilized. There is no upper limit to the amount of triazine, but it would be about 5000 ppm or about 4000 ppm or about 3000 ppm or about 2000 ppm or about 1000 20 ppm or about 500 ppm, based on the material to be stabilized.

The amount of the hydroxybenzophenone compound used in the material to be stabilized using the combination of additives of the present invention is also typically lower than normal usage. The lower limit of the amount of hydroxybenzophenone may be as low as about 10 ppm, or about 20 ppm, or about 50 ppm or about 75 ppm or about 100 ppm or 25 about 200 ppm, or about 500 ppm, based on the amount of material to be stabilized. There is no upper limit to the amount of hydroxybenzophenone, but it would be about 5000 ppm or about 4000 ppm or about 3000 ppm or about 2000 ppm or about 1000 ppm or about 500 ppm, based on the material to be stabilized.

The amount of the hindered amine compound used in the material to be stabilized 30 using the combination of additives of the present invention is more or less than its typically used amount. The lower limit of the amount of hindered amine compound may be about 250 ppm, or about 500 ppm, or about 1000 ppm or about 2000 ppm, based on the amount of material to be stabilized. There is no upper limit to the amount of hindered amine compound, but it would be about 30000 ppm, or about 20000 ppm or about 15000 ppm or 35 about 12500 ppm or about 10000 ppm or about 7500 ppm, or about 5000 ppm, based on the material to be stabilized.

The amount of hindered amine compound with respect to the other UV absorbers is typically greater. The ratio of hindered amine compound to the triazine UV absorber may be as high as about 50:1, or about 25:1, or about 20:1 or about 10:1, or about 7:1 or about 3:1. The ratio of hindered amine compound to the hydroxybenzophenone UV absorber 5 may be about 25:1, or about 20:1 or about 10:1, or about 7:1 or about 3:1 or about 2:1 or about 1.5:1 or about 1:1. The ratio of hydroxybenzophenone compound to the triazine UV absorber may be about 10:1, or about 5:1, or about 3:1 or about 2:1, or about 1:1 or about 1:2.

It should be noted that the amounts and ratios disclosed for the above additives are 10 each independent of each other.

This invention contemplates that a benzotriazole UV absorber may be substituted for the hydroxybenzophenone UV absorber. The benzotriazole compound may also be added to the other three additives. The same ratios and amounts disclosed above for the hydroxybenzophenone UV absorber may be used for the benzotriazole UV absorber. The 15 following are examples of benzotriazole UV absorbers: 2-(2-hydroxy-5-methylphenyl)-benzotriazole; 2-(2-hydroxy-5-tert-butylphenyl)-benzotriazole; 2-(2-hydroxy-3,5-di-tert-butylphenyl)-benzotriazole; 5-chloro-2-(2-hydroxy-3-tert-butyl-5-methylphenyl)-benzotriazole; 5-chloro-2-(2-hydroxy-3,5-di-tert-butyl-5-methylphenyl)-benzotriazole; 2-(2-hydroxy-3-tert-phenyl-5-methyl)-benzotriazole; 2-(2-hydroxy-3,5-di-tert-amyl)-benzotriazole; 20 2-(2-hydroxy-3-sec-butyl-5-tert-butyl)-benzotriazole; 2-(2-hydroxy-4-octyloxy)-benzotriazole; 2-(2-hydroxy-5-tert-octyl)-benzotriazole; 2-[2-hydroxy-3,5-di(α , α -dimethylbenzyl)phenyl]-benzotriazole; 2-(2-hydroxy-3-dodecyl-5-methylphenyl)benzotriazole; 2-[2-hydroxy-3-(α , α '-dimethylbenzyl)-5-(1,1,3,3-tetramethylbutyl)phenyl]benzotriazole; 2,2'-methylenebis[4-25 (1,1,3,3-tetramethylbutyl)-6-benzotriazol-2-ylphenol]; 2,[2-hydroxy-3-(3,4,5,6-tetrahydronaphthalimidomethyl)-5-methylphenyl]benzotriazole; 2-[3-tert-butyl-5-(2-(2-ethylhexyloxy carbonylethyl))-2-hydroxyphenyl]benzotriazole; a mixture of transesterification products of 2-[(3-tert-butyl-5-(2-methoxycarbonylethyl))-2-hydroxyphenyl]benzotriazole with polyethylene glycol of about MW 300; 5-chloro-2-[2-hydroxy-3-tert-butyl-5-(2-octyloxy carbonyl)ethylphenyl]benzotriazole.

30 This invention also includes a method of preparing the compositions above by contacting the UV stabilizing additive composition with the material to be stabilized. The material to be stabilized and UV stabilizing additive composition are contacted by preferably blending or compounding the components in a kneading apparatus such as a single or twin screw extruder, Banbury mixer, or hot rollers. The processing parameters and the use of 35 such kneading apparatuses are well known to those skilled in the art.

As would be apparent to those skilled in the art of making plastic materials, in addition to the material to be stabilized and UV stabilizing additive composition, the composition of the present invention may include conventional additives including but are not limited to, antioxidants, metal deactivators, hydroxylamines, nitrones, lactones, co-
5 stabilizers, nucleating agents, clarifying agents, neutralizers, metallic stearates, metal oxides, hydrotalcites, fillers and reinforcing agents, plasticizers, lubricants, emulsifiers, pigments, rheological additives, catalysts, leveling agents, optical brighteners, flame retardant agents, anti-static agents and blowing agents and combinations thereof.

The UV stabilizing additive composition and the material to be stabilized may be
10 used to make articles, such as an extruded or molded articles, coatings, tapes and films. The articles may be formed by extrusion, sheet extrusion, injection molding, blow molding, injection blow molding, rotational or roto-molding, calendering, thermoforming, compression molding, vacuum molding, pressure molding, reaction injection molding, and other similar techniques known in the art. In addition, coatings may be applied by
15 powder coating, extrusion coating, electrocoating, spraying, dipping, and other similar techniques known in the art.

EXAMPLES

20 The following examples are provided to illustrate the present invention. The examples are not intended to limit the scope of the present invention and they should not be so interpreted.

25 **Examples 1 to 4. Gloss retention, Retained Elongation and Retained Tensile Strength in a Low Density Polyethylene (LDPE) composition**

The UV additives of Examples 1 to 4 are mixed by using a dry blending technique. In addition to the additives, an antioxidant package containing 0.04% by weight (1,3,5-tris-(3,5-di-tert-butyl-4-hydroxybenzyl)-s-triazine- 2,4,6(1H,3H,5H)trione),
30 0.08% of tris(2,4-di-tert-butylphenyl)phosphite (Cytec Industries Inc., W. Paterson, NJ) and 0.05% by weight zinc stearate are also mixed with the UV additives. These additives are compounded with low density polyethylene from Equistar, Houston TX (Microthene, MI = 3.6, density = 0.9395 g/mL) and extruded using a Davis Standard Killion with conventional single-screw extrusion parameters. After extrusion, standard 2
35. x 2.5 x 0.125 inch plaques are injection molded using an Arburg injection molder.

The performance criteria of Gloss retention, Retained Elongation and Retained Tensile Strength are measured at set exposure intervals (500 for gloss and 2500 hours

for retained elongation and tensile strength) using accelerated exposure in a xenon weather-ometer under ASTM-G-26 with water spray testing conditions. Prior to gloss and color measurements, the samples are washed with DI water and wiped.

5 Gloss retention measurements are conducted on a Gardner instrument under
ASTM Test Procedure D523 with a 60° angle.

For breaking strength, 5 tensile bars per each data point are tested on an Instron Engineering Company Tensile Tester (Series IX Automated Test System 7.51.00). The average tensile breaking strength of the three test samples are measured and normalized to samples that are not UV exposed to give a % breaking strength. The
10 cross-head speed of the tensile tester is 1 inch (0.254 cm.) per minute.

The results are shown in Tables 1 to 3 below.

Table 1. Percent Gloss Retention of Examples 1 to 4

Example	Description	% gloss retention 3500 hours	% gloss retention 4500 hours
1	0.900% of UV-3346, 0.045%UV-1164, 0.045% UV-531	87	71
2	0.900% of UV-3346, 0.090% of UV-531	67	44
3	0.900% of UV-3346, 0.090% of UV-1164	91	75
4	1.0 % of UV-3346	67	52

15 Cyasorb® UV 3346 is 1,6-hexamethylene, N,N'-bis(2,2,6,6-tetramethyl-4-piperidinyl)-, Polymers with morpholine-2,4,6-trichloro-1,3,5-triazine (HALS),
Cyasorb® UV 1164 is 2-[4,6-bis(2,4-dimethylphenyl)-1,3,5-triazin-2-yl]-5-(octyloxy) phenol (triazine UV absorber),
Cyasorb® UV 531 is 2-hydroxy-4-n-octoxybenzophenone(UV absorber).

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Table 2. Retained Tensile Strength of Examples 1 to 4

Example	Description	% Retained Tensile Strength 2500 hours	% Retained Tensile Strength 5000 hours
1	0.900% of UV-3346, 0.045%UV-1164, 0.045% UV-531	87%	84%
2	0.900% of UV-3346, 0.090% of UV-531	90%	76%
3	0.900% of UV-3346, 0.090% of UV-1164	90%	77%
4	1.0 % of UV-3346	73%	69%

Table 3. Retained Elongation of Examples 1 to 4

Example	Description	% Retained Elongation 2500 hours	% Retained Elongation 5000 hours
1	0.900% of UV-3346, 0.045%UV-1164, 0.045% UV-531	71%	71%
2	0.900% of UV-3346, 0.090% of UV-531	82%	60%
3	0.900% of UV-3346, 0.090% of UV-1164	69%	64%
4	1.0 % of UV-3346	49%	45

The results demonstrate that additive compositions containing half the amount of a triazine UV absorber with a benzophenone perform better than compositions containing the triazine UV alone at double loading.

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